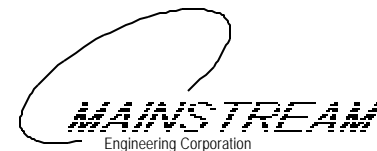


# *Advanced Testing of Safe-Solvent Replacements for CFC-113 For Use in Cleaning Oxygen Systems*

*Lawrence R. Grzyll, John A. Meyer,  
and Dwight D. Back*

*Mainstream Engineering Corporation  
Rockledge, Florida 32955*

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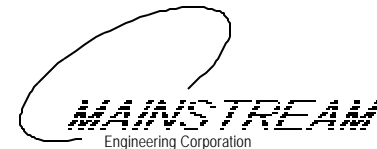


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# *Background*

- *Use and Production of CFC-113 Restricted*
- *Replacement Cleaning Solvent Needed*
  - *Solvency As Good or Better Than CFC-113*
  - *Non-Flammable*
  - *Compatible With Liquid and Gaseous Oxygen*
  - *Low Toxicity or Non-Toxic*
  - *Acceptable Environmental Properties*
  - *Similar Volatility and Other Physical Properties*
  - *Manufacturable at Reasonable Cost*

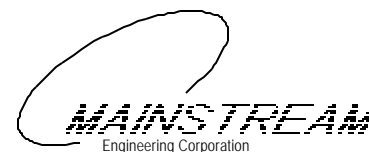
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# *Phase I Compound Screening*

- *Screened 247 Untested Halogenated Compounds*
  - *Solubility Parameter Solvency Screening Property*
    - *Predicted Using Structure-Property Relationships (SPRs)*
    - *Compounds With Similar Solubility Parameters Have Similar Solvency*
  - *Other SPRs Used to Predict Atmospheric Properties, Toxicity, Boiling Point*
- *5 Pure Compounds and 3 Mixtures Recommended*
  - *Solvency and Materials Compatibility Tests Performed*

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# Solvent Candidates

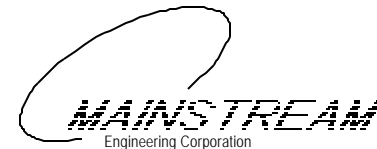
## ■ Solvent Candidates

- 4-bromo-3-chloro-3,4,4-trifluoro-1-butene,  $\text{CH}_2=\text{CH}-\text{CFCl}-\text{CF}_2\text{Br}$
- 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether,  $\text{CHF}_2-\text{O}-\text{CHCl}-\text{CF}_3$
- 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether,  $\text{CHF}_2-\text{O}-\text{CF}_2-\text{CHFCl}$
- methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether,  $\text{CH}_3-\text{O}-\text{CH}-(\text{CF}_3)_2$
- 1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene,  $\text{CHBr}=\text{C}-(\text{CF}_3)_2$
- mixtures of  $\text{CH}_2=\text{CH}-\text{CFCl}-\text{CF}_2\text{Br}$  and  $\text{CHF}_2-\text{O}-\text{CHCl}-\text{CF}_3$

## ■ Baseline Solvents For Comparison

- 1-iodononafluorobutane,  $\text{CF}_2\text{I}-\text{CF}_2-\text{CF}_2-\text{CF}_3$  (Ikon P)
- 1,3-dichloro-1,1,2,2,3-pentafluoropropane,  $\text{CF}_2\text{Cl}-\text{CF}_2-\text{CHFCl}$  (AK-225G)
- CFC-113,  $\text{CFCl}_2-\text{CF}_2\text{Cl}$

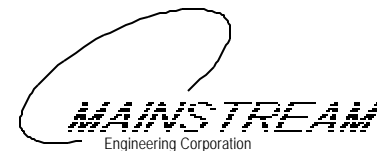
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# Objectives

- *Perform Solvency Tests Against Selected Contaminants*
- *Determine Compatibility With Liquid and Gaseous Oxygen*
- *Measure Flammability*
- *Determine Atmospheric Impact*
- *Determine Toxicity Characteristics*
- *Measure Key Thermophysical Properties*
- *Recommend Replacement Solvent*
- *Determine Cleaning Effectiveness in an Oxidizer System*
- *Assess Manufacturability of Recommended Solvent*

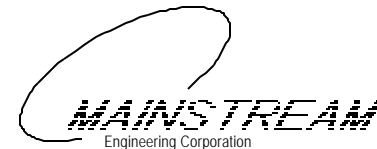
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# Solvency Tests

- *Apply Approximately 0.1 grams of Contaminant on 1" Square Stainless Coupon*
- *Clean Static and Using Ultrasonics in 15 ml. of Solvent*
- *Mass of Contaminant Removed Determined By Weight Difference of Coupon Before and After Cleaning*
- *Most Solvent Candidates Cleaned As Good or Better Than CFC-113*
- *Selected Contaminants:*
  - *Mil-Spec 83232 Hydraulic Oil*
  - *Mil-Spec 7808 Engine Oil*
  - *Mil-Spec 81322 Hydrocarbon Grease*
  - *Krytox*
  - *Simple Green Aqueous Cleaner*

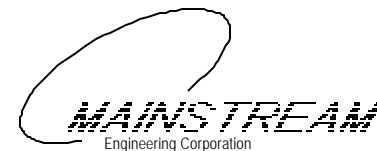
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# *Compatibility With Gaseous Oxygen*

- *ASTM G72, “Standard Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen Enriched Environment”*
  - *AIT < 250°F, Not Recommended for O<sub>2</sub> Systems*
  - *AIT 250°F - 400°F, Use Caution in O<sub>2</sub> Systems*
  - *AIT > 400°F, Recommended for O<sub>2</sub> Systems*
- *Performed by Wendell Hull & Associates*

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# *GO<sub>2</sub> Compatibility Results*

Solvent	Average AIT	Category
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	451°F	Recommended
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	725°F	Recommended
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	378°F	Caution
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	390°F	Caution
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	464°F	Recommended
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)	no ignition @ 50 psia and 2000 psia	Recommended
1-iodononafluorobutane (Ikon P)	345-355°F @ 2000 psia	Caution
1,3-dichloro-1,1,2,2,3-pentafluoropropane (AK-225)	no ignition @ 50 psia and 2000 psia	Recommended

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# *Compatibility With Liquid Oxygen*

- *ASTM G86, “Standard Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Pressurized Oxygen Environments”*
  - *Pass if No Reactions in 20 Impacts*
  - *Pass if Not More Than One Reaction in 60 Impacts*
- *Performed By NASA-WSTF Personnel*

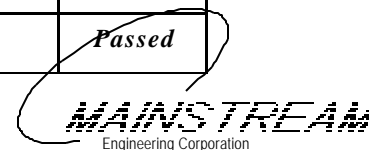
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# LOX Compatibility Results

Solvent	Results	Category
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	1 Reaction/60 Impacts	<i>Passed</i>
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	2 Reactions/28 Impacts	<i>Failed</i>
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	2 Reactions/10 Impacts	<i>Failed</i>
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	<i>Passed</i>
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	<i>Passed</i>
25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	1 Reaction/60 Impacts	<i>Passed</i>
50% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene 50% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	<i>Passed</i>
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)		<i>Passed</i>
1-iodononafluorobutane (Ikon P) (Taken From Reference 4)	2 Reactions/17 Impacts	<i>Failed</i>
1,3-dichloro-1,1,2,2,3-pentafluoropropane (AK-225)		<i>Passed</i>

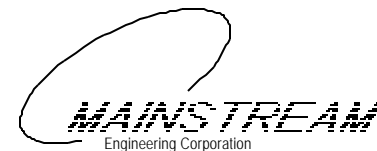
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# *Flammability Tests*

- *ASTM D93, “Standard Test Method for Flash Point by Pensky-Martens Closed Tester”*
- *Performed By Mainstream*
- *No Flash Points Observed For Candidate Solvents or Baseline Solvents*

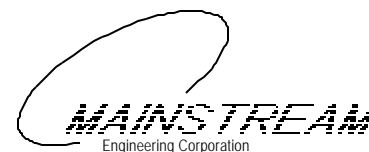
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# *Atmospheric Impact*

- *Some Information Found In Open Literature*
- *Compounds With Unknown Information  
Tested By Dr. Vladimir Orkin of NIST*
  - *Measured Reactivity Toward Hydroxyl Radicals  
(Atmospheric Lifetime)*
  - *Measure UV Absorption Cross Section  
(ODP and GWP)*

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# *Atmospheric Properties*

Compound	ODP	GWP	Atmospheric Lifetime
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0.004-0.03	200	2-5.9 yrs.
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	0.004-0.04	330	2.4-8.2 yrs.
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	0.00014-0.012	< 10	4.2 days
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	0	13 - 43	65 days
CFC-113	0.9	5000	85 yrs.
Ikon-P	< 0.0025	< 2	2 days
AK-225	0.02-0.03	170-530	6.6 yrs.

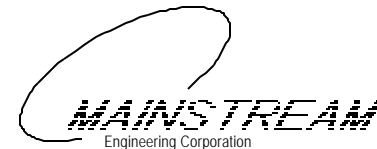
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# *Toxicity Characteristics*

- *Ames Test For Mutagenicity*
- *Acute Skin Irritation (Rabbit)*
- *Acute Oral Toxicity (Rat)*
- *Tests Performed By ST&T Consultants*
  - *Performed per Good Laboratory Practice (GLP)*

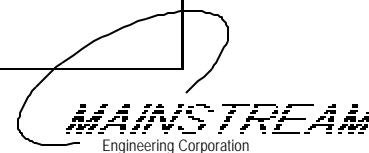
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# Toxicity Properties

Compound	LD50	Ames	Dermal Irritation Index
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	8.1 g/kg	negative	0.2
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	13.0 g/kg	negative	0.08
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	> 40 g/kg	negative	2.13
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	> 40 g/kg	negative	0.25
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	0.1 g/kg	negative	1.33
CFC-113	43 g/kg	negative	mild irritant
Ikon-P	no data	negative	mild irritant
AK-225	> 5 g/kg	negative	no data
<p>Dermal Irritation Index</p> <p>3.0-4.9 = potential for severe irritation</p> <p>2.0-2.9 = potential for moderate irritation</p> <p>1.0-1.9 = potential for mild irritation</p> <p>0.1-0.9 = potential for slight irritation</p> <p>&lt;0.1 = no irritation potential</p>			

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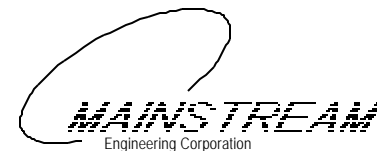




# *Recommend Solvent Replacement*

- *Ranking Scheme Developed Based On Properties Studied*
  - *Cost Included in Ranking*
- *Mixture of 25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene and 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether Recommended*

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# *Key Physical Properties*

- *Measured At 25°C By Mainstream*
  - *Liquid Density*
  - *Liquid Viscosity*
  - *Surface Tension*
  - *Vapor Pressure*
  - *Boiling Range*
  - *Freezing Point*

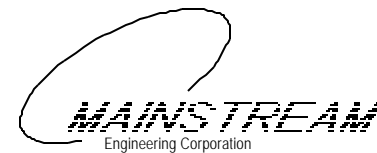
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## *Key Physical Props. At 25°C*

Property	Value
Liquid Density	1.53 g/ml
Liquid Viscosity	0.554 cP
Surface Tension	17.1 dyne/cm
Vapor Pressure	264 mm Hg
Boiling Range	55-96°C
Freezing Point	< -127°C

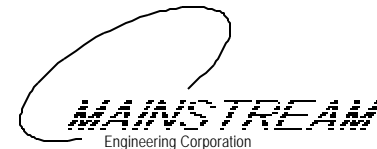
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# *Cleaning An Oxidizer System*

- *Air Force Oxidizer System Sent to Mainstream*
- *Procedure Based on NASA WSTF Cleaning Studies*
- *Contaminants:*
  - *Krytox GPL 224*
  - *83282 Hydraulic Oil*
  - *7808 Hydraulic Grease*
  - *81322 Hydrocarbon Grease*
  - *2 Solutions Prepared: 0.95 and 1.6 grams of Each Contaminant Dissolved in CFC-113*
  - *32 ml. of Solution Introduced to System*

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## *Photograph of System*



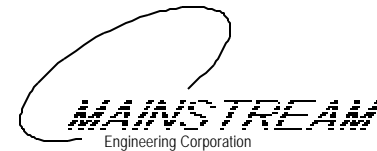
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# *Cleaning Results*

<b>Contaminant Solution</b>	<b>CFC-113 Results</b>	<b>Mainstream Solvent Blend Results</b>
Dilute (0.95 grams each contaminant)	80.3 % Removal	89.6 % Removal
Concentrated (1.56 grams each contaminant)	90.6 % Removal	74.0 % Removal

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# *Assess Manufacturability*

- *Patent Application Filed With USPTO*
- *Mainstream's Estimated Delivery Price:*
  - *\$185/gallon at 500 gallons per month*
- *Technology Spun-off Into HVAC&R Industry*
  - *Flushing Solvent*
  - *Leak Detector For Furnace Heat Exchangers*
  - *Sensitive Refrigerant Leak Detector*

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# Conclusions

- *Replacement Solvent For CFC-113 For Cleaning Oxygen Systems Identified*
  - *Superior to CFC-113 in Coupon Solvency Tests*
  - *Similar to CFC-113 in Cleaning Oxygen Systems*
  - *Acceptable Toxicity and Atmospheric Properties*
  - *Non-Flammable and Oxygen Compatible*
  - *Affordable Cost*
  - *Spin-off Commercial Applications in HVAC&R Industry*

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